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(54) CATHODE ELECTRODE CATALYST FOR FUEL CELL AND METHOD OF MANUFACTURING THE SAME

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a cathode electrode catalyst for a fuel cell and the method of manufacturing the same, which can allow the speed of reduction reaction of oxygen in the cathode to increase.
SOLUTION: At least one selected from a group comprising of Sb2O4 and CeO2 is carried to a carrier carrying Pt or Pt-Mo alloy.

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CLAIMS

[Claim(s)]
[Claim 1] The cathode electrode catalyst for fuel cells characterized by making the support which supported the Pt-Mo alloy support at least 1 chosen from the group who consists of Sb2O4 and CeO2, and growing into it.
[Claim 2] The cathode electrode catalyst for fuel cells characterized by making the support which supported Pt support CeO2, and growing into it.
[Claim 3] The manufacture approach of the cathode electrode catalyst for fuel cells characterized by acquiring the cathode electrode catalyst for fuel cells which sinks into a cerium solution, calcinates Pt-Mo alloy support support at 150-200 degrees C in air, and consists of Pt-Mo alloy-CeO2 support support.
[Claim 4] The manufacture approach of the cathode electrode catalyst for fuel cells characterized by acquiring the cathode electrode catalyst for fuel cells which sinks Pt support support into a cerium solution, calcinates this Pt support support at 150-200 degrees C in air, and consists of Pt-CeO2 support support.
[Claim 5] The manufacture approach of the cathode electrode catalyst for fuel cells characterized by acquiring the cathode electrode catalyst for fuel cells which consists of Pt-Mo alloy-CeO2 support support or Pt-CeO2 support support by mixing mechanically Pt-Mo alloy support support or Pt support support with the shape 2 of a particle CeO.
[Claim 6] The manufacture approach of the cathode electrode catalyst for fuel cells characterized by acquiring the cathode electrode catalyst for fuel cells which calcinates 2OSb3 powder in air above 500 degrees C, is mixed with Pt-Mo alloy support support on a machine target, and consists of Pt-Mo alloy-Sb2O4 support support.

[Translation done.]

* NOTICES *

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the cathode electrode catalyst for fuel cells, and its manufacture approach.
[0002]
[Description of the Prior Art] The fuel cell has acquired electromotive force by the cell reaction which obtains water from hydrogen and oxygen. The hydrogen of a raw material makes a original fuel and water, such as a methanol, react to the bottom of existence of a reforming catalyst, and is obtained. It is observed as what can demonstrate the engine performance in which the polymer electrolyte fuel cell (PEFC:Polymer Electrolyte Fuel Cell) was excellent especially among such fuel cells. That is, in the polymer electrolyte fuel cell, hydrogen was used as the fuel and electromotive force has been acquired according to the electrode reaction in an anode (fuel electrode) and a cathode (air pole). The reduction reaction of oxygen has occurred with the cathode here. However, it is surmised that this reduction reaction is slow and constitutes the rate-determining step of electrode reaction. The platinum catalyst is used for the electrode reaction in this cathode in many cases. To improve the catalyst engine performance of this platinum catalyst was desired. This was the same at other fuel cells, such as a phosphoric-acid mold (PAFC) fuel cell.
[0003]
[Problem(s) to be Solved by the Invention] This invention was made to the above-mentioned situation, and aims at offering the cathode electrode catalyst for fuel cells it was made to raise the rate of the reduction reaction of the oxygen in a cathode, and its manufacture approach.
[0004]
[Means for Solving the Problem] In order to attain the above-mentioned purpose, the cathode electrode catalyst for fuel cells concerning this invention is characterized by making the support which supported the Pt-Mo alloy support at least 1 chosen from the group who consists of Sb2O4 and CeO2, and growing into it. This invention is a cathode electrode catalyst for fuel cells, and contains what supported CeO2 in the support which supported Pt as the one gestalt.
[0005] This invention is the manufacture approach of the cathode electrode catalyst for fuel cells as another side face, it sinks into a cerium solution, calcinates Pt-Mo alloy support support at 150-200 degrees C in air, and is characterized by acquiring the cathode electrode catalyst for fuel cells which consists of Pt-Mo alloy-CeO2 support support.
[0006] Moreover, the manufacture approach of the cathode electrode catalyst for fuel cells concerning this invention sinks Pt support support into a cerium solution, calcinates this Pt support support at 150-200 degrees C in air, and can carry it out also as a gestalt which acquired the cathode electrode catalyst for fuel cells which consists of Pt-CeO2 support support. Pt-Mo alloy-CeO2 support support or Pt-CeO2 support support is obtained also by mixing mechanically Pt-Mo alloy support support or Pt support support with the shape 2 of a particle CeO.
[0007] Furthermore, the manufacture approach of the cathode electrode catalyst for fuel cells concerning this invention is another gestalt, and 2OSb3 powder is calcinated in air above 500 degrees C, and he mixes with Pt-Mo alloy support support on a machine target, and is trying to obtain Pt-Mo alloy-Sb2O4 support support. Although this invention is suitable for a polymer electrolyte fuel cell, otherwise, it is also applicable to fuel cells, such as a phosphoric acid fuel cell.

[0008]
[Embodiment of the Invention] Hereafter, the cathode electrode catalyst for fuel cells concerning this invention and its manufacture approach are further explained to a detail about the gestalt of the operation etc.
[0009] In the fuel cell, it has the platinum catalyst layer by the side of a fuel electrode, and the platinum catalyst layer by the side of an air pole on both sides of the solid-state poly membrane as a gestalt of the 1 operation. Here, the following reactions are performed in an anode (fuel electrode) and a cathode (air pole).
[0010] The following reactions are made to cause by the platinum catalyst layer in an anode.
H2 -> 2H++2e - H+ produced by this reaction is spread. On the other hand, the following reactions are made to cause by the platinum catalyst layer in a cathode.
2H++2e-+1 / 2O2 -> H2O -- these reactions are doubled, a cell reaction is constituted and electromotive force can be acquired.
[0011] Here, as described above, resistance of the reduction reaction of the air by the side of a cathode is considered to constitute the rate-determining step greatly. This inventions found out that such resistance decreased sharply by using the co-catalyst of at least 1 chosen from the group who consists of Sb2O4 and CeO2 further, as a result of examining wholeheartedly the electrode catalyst using the Pt-Mo alloy used for a platinum catalyst layer. Although not completely supported about the principle, it is thought that it calls at the place mostly explained below about drawing 1 . As shown in drawing 1 , the oxygen molecule 3 is first captured by the co-catalyst particle 2 on the support particle 1. This oxygen molecule 3 is lengthened by Mo component in the particle 4 of a Pt-Mo alloy, and carries out spillover to the Pt-Mo alloy particle 4. The catalyst property of Pt component is demonstrated by this and the reduction reaction of oxygen advances promptly by it. In addition, when making Sb 2O4 into a co-catalyst, this invention persons will check the effectiveness of resistance reduction only by supporting to the ability not checking effectiveness on the support which supported only Pt with CeO2, if they are not Pt-Mo alloys. Therefore, like the mechanism of drawing 1, when CeO2 is used, it is guessed that the spillover of oxygen is what advances even if there is no Mo.
[0012] The powder of said support has desirable carbon powder, for example, a graphite, carbon black, the activated carbon that has electric conductivity can be mentioned. Especially, for the electrode catalyst for fuel cells, KETCHIEN carbon and Balkan Peninsula carbon are desirable.
[0013] As for the ratio of the Pt-Mo alloy in Pt-Mo alloy support carbon when a Pt-Mo alloy is used and the ratio of Mo in the Pt-Mo alloy content contained in the cathode electrode catalyst for fuel cells supports a 1-99-mol % and Pt-Mo alloy to carbon, it is desirable that it is 1 - 99wt%. Moreover, when using a Pt-Mo alloy, the amount of support of CeO2 and Sb 2O4 as a co-catalyst has 0.01 to 10 desirable times to the weight of Pt-Mo alloy support carbon.
[0014] When using not a Pt-Mo alloy but Pt, as for the ratio of Pt in Pt support carbon at the time of supporting Pt to carbon, it is desirable that it is 1 - 99wt%. Moreover, when using Pt, the amount of support of CeO2 and Sb 2O4 as a co-catalyst has 0.01 to 10 desirable times to the weight of Pt support carbon.
[0015] Subsequently, about the manufacture approach of the cathode electrode catalyst for fuel cells concerning this invention, the case where a catalytic activity component is supported is mentioned to carbon support, and the gestalt of the operation is explained.
[0016] Pt solution is prepared so that the molar quantity of Pt may turn into a predetermined amount. As a Pt solution, H2PtCl6 solution and Pt complex ion solution of Pt(NO2)2(NH3) 2 grade can be mentioned. It mixes in the water / ethanol mixed solution which boiled this Pt solution, and Pt ion is returned. Carbon powder, such as KETCHIEN carbon used as the carbon support after cooling, is added, and carbon powder is made to carry out adsorption support of the Pt. Then, it filters and dries, and heat-treats in a hydrogen ambient atmosphere, and Pt support carbon is obtained.
[0017] Next, it sinks into molybdenum water solutions, such as 5 molybdenum chloride water solutions 0.1 to 2 twice the amount of Mo of the number of mols of Pt, Pt support carbon is returned to them at 250 degrees C - 800 degrees C by hydrogen, and Pt-Mo alloy support carbon is obtained. Next, it sinks into PtMo support carbon and cerium water solutions, such as a cerium-nitrate water solution, are calcinated at 150-200 degrees C among air so that 0.01 to 10 times as many CeO2 as

this may be included to the weight of Pt, and Pt-Mo alloy-CeO2 support carbon is obtained.
[0018] If it sinks into Pt support carbon and cerium water solutions, such as a cerium-nitrate water solution, are calcinated at 150-200 degrees C in air so that 0.01 to 10 times as many CeO2 as this may be included to the weight of Pt above, without supporting Mo, Pt-CeO2 support carbon can be obtained.
[0019] Moreover, instead of CeO2 after obtaining Pt-Mo alloy support carbon, Sb 2O4 is made to support and it is a Pt-Mo alloy. - Sb 2O4 Support carbon can be obtained. In this case, 2OSb3 powder (particle size of 0.1 micrometers or less) can be calcinated in air above 500 degrees C so that it may be set to 0.01 to 10 times as much Sb 2O4 as the weight of Pt-Mo alloy support carbon, and it can mix with Pt-Mo alloy support carbon on a machine target, and Pt-Mo alloy-Sb2O4 support carbon can be obtained. If it carries out to baking and coincidence of Sb 2O4 in 500 degrees C or more, it will mix for a carbon component burning out mechanically.
[0020] In addition, a commercial item can also be used for Pt support carbon (Pt/C) and Pt-Mo alloy support carbon (PtMo/C) as it is. It can mix mechanically to Pt-Mo alloy support carbon, and Pt-Mo alloy-CeO2 support carbon can also acquire the shape 2 of a particle CeO to it.
[0021]
[Example] H2PtCl6 solution (Pt content of 100g/l.) was diluted to 1g metal / l so that the molar quantity of example 1Pt might be set to 0.6mmol(s). The solution (1440g [of ion exchange water] and ethanol 1140g and polyvinyl alcohol 0.4g) was boiled. This boiling solution was made to add and carry out the reaction of the Pt ion solution prepared previously for 15 minutes (usually 10 minutes - 24 hours), and Pt ion was returned to it. 120mg (KETCHIEN carbon whose specific surface area is 800m2/g) of carbon powder was added and stirred after cooling, and carbon was made to carry out adsorption support of the Pt. Then, it filtered and dried, and in the hydrogen ambient atmosphere, heat treatment was carried out for 1 hour (usually 0.5 - 6 hours), pyrolysis removal of the polyvinyl alcohol was carried out, and 250 degrees C of Pt support carbon catalysts were acquired. Next, it sank into 5 molybdenum chloride water solutions 1 time (usually 0.1 to 2 twice) the amount of Mo of the number of mols of Pt, Pt support carbon was returned to them by hydrogen at 500 degrees C (usually 250 degrees C - 800 degrees C), and Pt-Mo alloy support carbon was obtained. Next, it sank into Pt-Mo alloy support carbon, the cerium-nitrate water solution was calcinated at 200 degrees C among air, and Pt-Mo alloy-CeO2 support carbon was obtained.
[0022] H2PtCl6 solution (Pt content of 100g/l.) was diluted to 1g metal / l so that the molar quantity of example 2Pt might be set to 0.6mmol(s). The solution (1440g [of ion exchange water] and ethanol 1140g and polyvinyl alcohol 0.4g) was boiled. This boiling solution was made to add and carry out the reaction of the Pt ion solution prepared previously for 15 minutes (usually 10 minutes - 24 hours), and Pt ion was returned to it. 120mg (KETCHIEN carbon whose specific surface area is 800m2/g) of carbon powder was added and stirred after cooling, and carbon was made to carry out adsorption support of the Pt. Then, it filtered and dried, and in the hydrogen ambient atmosphere, heat treatment was carried out for 1 hour (usually 0.5 - 6 hours), pyrolysis removal of the polyvinyl alcohol was carried out, and 250 degrees C of Pt support carbon catalysts were acquired. Next, it sank into Pt support carbon and the cerium-nitrate water solution was calcinated at 200 degrees C among air so that twice (usually 0.01 to 10 times) as many CeO2 as this might be included to the weight of Pt, and Pt-CeO2 support carbon was obtained.
[0023] H2PtCl6 solution (Pt content of 100g/l.) was diluted to 1g metal / l so that the molar quantity of example 3Pt might be set to 0.6mmol(s). The solution (1440g [of ion exchange water] and ethanol 1140g and polyvinyl alcohol 0.4g) was boiled. This boiling solution was made to add and carry out the reaction of the Pt ion solution prepared previously for 15 minutes (usually 10 minutes - 24 hours), and Pt ion was returned to it. 120mg (KETCHIEN carbon whose specific surface area is 800m2/g) of carbon powder was added and stirred after cooling, and carbon was made to carry out adsorption support of the Pt. Then, it filtered and dried, and in the hydrogen ambient atmosphere, heat treatment was carried out for 1 hour (usually 0.5 - 6 hours), pyrolysis removal of the polyvinyl alcohol was carried out, and 250 degrees C of Pt support carbon catalysts were acquired. Next, it sank into 5 molybdenum chloride water solutions 1 time (usually 0.1 to 2 twice) the amount of Mo of the number of mols of Pt, Pt support carbon was returned to them at 250 degrees C - 800 degrees C by hydrogen, and Pt-Mo alloy support carbon was obtained. Next, 2OSb3 powder (particle size of

0.1 micrometers or less) was calcinated in air above 500 degrees C so that it might be set to twice (usually 0.01 to 10 times) as many Sb 2O4 as the weight of Pt-Mo alloy support carbon, and it mixed with Pt-Mo alloy support carbon on the machine target, and Pt-Mo alloy-Sb2O4 support carbon was obtained.
[0024] The polymer electrolyte fuel cell was manufactured using the cathode electrode catalyst of example 4 examples 1-3, the trial was performed, and the generation-of-electrical-energy engine performance was evaluated.
[0025] (Preparation of a cell cel) The Nafion solution was added as a polyelectrolyte solution for the anode electrode catalyst (PtRu alloy support carbon) at water / ethanol mixed liquor list, and the slurry was prepared by ultrasonic stirring. The obtained slurry was applied to the Teflon (trademark) sheet, it imprinted on one side of the solid-state poly membrane (at the Du Pont make, a trade name is the Nafion film) of 50 micrometers of thickness, and the anode pole was formed. The amount of Pt (s) in an anode pole was 0.5 mg/cm2, the amount of Ru was 0.5 mg/cm2, and the amount of Nafion was 1 mg/cm2.
[0026] On the other hand, the Nafion solution was added as a polyelectrolyte solution for the cathode electrode catalyst of examples 1-3 at water / ethanol mixed liquor list, and the slurry was prepared by ultrasonic stirring. It imprinted to the field which applied the obtained slurry to the Teflon sheet and imprinted the anode of the solid-state poly membrane (a trade name is the Nafion film at the Du Pont make) of 50 micrometers of thickness, and the field of the opposite side, and the cathode pole was formed. The amount of Pt(s) in a cathode pole was 0.5 mg/cm2, and the amount of Nafion was 0.5 mg/cm2. After sticking carbon paper on an anode pole and each cathode pole, these were inserted with one pair of separators, and the electrode cel of 5cm around was produced.
[0027] <Generation-of-electrical-energy performance evaluation> About the obtained electrode cels 1-3, a generation-of-electrical-energy trial is performed by the test condition explained below, and the result is shown in the following table 1.
[0028] anode side: -- an H2 60%, CO2 20%, and N2 20% side and a ppm, 2ata, temperature [of 80 degrees C], and 80% cathode [of CO10 hydrogen utilization factors] side -- :air (Air), 2ata, the temperature of 80 degrees C, and 40% [Table 1] of air utilization rates

	0.15A/cm2	0.35A/cm2	0.7A/cm2
電極1	0.80 V	0.75 V	0.65 V
電極2	0.80 V	0.75 V	0.65 V
電極3	0.82 V	0.76 V	0.66 V
従来電極	0.78 V	0.70 V	0.60 V

[0029] Compared with a cel, it turns out conventionally that the electrode cels 1-3 using the prototype catalysts 1-3 are highly efficient so that clearly from Table 1. In addition, the above-mentioned example followed the polymer electrolyte fuel cell. However, this invention is not limited to such a thing and can be applied to other fuel cells, such as a phosphoric acid fuel cell.
[0030]
[Effect of the Invention] According to this invention, the cathode electrode catalyst for fuel cells it was made to raise the rate of the reduction reaction of the oxygen in a cathode, and its manufacture approach are offered so that clearly from the above-mentioned place.

[Translation done.]

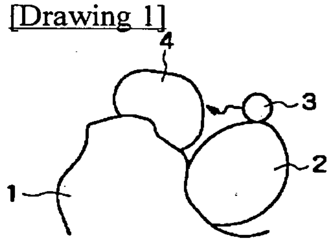
DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is a conceptual diagram explaining the mechanism of reduction of the oxygen in this invention.
[Description of Notations]
1 Support Particle
2 Co-catalyst Particle
3 Oxygen Molecule
4 Alloy Particle

[Translation done.]

DRAWINGS

[Drawing 1]



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最終頁に続く

(54)【発明の名称】　燃料電池用カソード電極触媒およびその製造方法

(57)【要約】
【課題】　カソードにおける酸素の還元反応の速度を上昇させるようにした燃料電池用カソード電極触媒およびその製造方法を提供する。
【解決手段】　ＰｔまたはＰｔ－Ｍｏ合金を担持した担体に、Sb_2O_4とCeO_2から成るグループから選択した少なくとも一を担持させた。

【特許請求の範囲】

【請求項1】　Pt－Mo合金を担持した担体に、Sb_2O_4とCeO_2から成るグループから選択した少なくとも一を担持させて成ることを特徴とする燃料電池用カソード電極触媒。

【請求項2】　Ptを担持した担体に、CeO_2を担持させて成ることを特徴とする燃料電池用カソード電極触媒。

【請求項3】　Pt－Mo合金担持担体をセリウム溶液に含浸し、空気中で150～200℃で焼成し、Pt－Mo合金－CeO_2担持担体から成る燃料電池用カソード電極触媒を得ることを特徴とする燃料電池用カソード電極触媒の製造方法。

【請求項4】　Pt担持担体をセリウム溶液に含浸し、該Pt担持担体を空気中で150～200℃で焼成し、Pt－CeO_2担持担体から成る燃料電池用カソード電極触媒を得るようにしたことを特徴とする燃料電池用カソード電極触媒の製造方法。

【請求項5】　Pt－Mo合金担持担体またはPt担持担体を微粒子状CeO_2と機械的に混合することによって、Pt－Mo合金－CeO_2担持担体またはPt－CeO_2担持担体から成る燃料電池用カソード電極触媒を得るようにしたことを特徴とする燃料電池用カソード電極触媒の製造方法。

【請求項6】　Sb_2O_3粉末を500℃以上で空気中で焼成し、Pt－Mo合金担持担体と機械的に混合し、Pt－Mo合金－Sb_2O_4担持担体から成る燃料電池用カソード電極触媒を得るようにしたことを特徴とする燃料電池用カソード電極触媒の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、燃料電池用カソード電極触媒およびその製造方法に関するものである。

【0002】

【従来の技術】燃料電池は、水素と酸素から水を得る電池反応によって起電力を得ている。原料の水素は、メタノールなどの原燃料と水を改質触媒の存在下に反応させて得られる。このような燃料電池のうち、特に、固体高分子型燃料電池（PEFC：Polymer Electrolyte Fuel Cell）が優れた性能を発揮できるものとして注目されている。すなわち、固体高分子型燃料電池では、水素を燃料とし、アノード（燃料極）、カソード（空気極）における電極反応によって起電力を得ている。ここでカソードでは、酸素の還元反応が起こっている。しかし、この還元反応が遅く、電極反応の律速段階を構成していると推測される。このカソードにおける電極反応には、白金触媒が用いられていることが多い。かかる白金触媒の触媒性能を上げることが望まれていた。このことは、リン酸型（PAFC）燃料電池等の他の燃料電池でも同様であった。

【0003】

【発明が解決しようとする課題】本発明は上記事情に対してなされたもので、カソードにおける酸素の還元反応の速度を上昇させるようにした燃料電池用カソード電極触媒およびその製造方法を提供することを目的とする。

【0004】

【課題を解決するための手段】上記目的を達成するため、本発明に係る燃料電池用カソード電極触媒は、Pt－Mo合金を担持した担体に、Sb_2O_4とCeO_2から成るグループから選択した少なくとも一を担持させて成ることを特徴とする。本発明は、燃料電池用カソード電極触媒であって、Ptを担持した担体に、CeO_2を担持したものもその一形態として含む。

【0005】本発明は、別の側面として燃料電池用カソード電極触媒の製造方法であり、Pt－Mo合金担持担体をセリウム溶液に含浸し、空気中で150～200℃で焼成し、Pt－Mo合金－CeO_2担持担体から成る燃料電池用カソード電極触媒を得ることを特徴とする。

【0006】また、本発明に係る燃料電池用カソード電極触媒の製造方法は、Pt担持担体をセリウム溶液に含浸し、該Pt担持担体を空気中で150～200℃で焼成し、Pt－CeO_2担持担体から成る燃料電池用カソード電極触媒を得るようにした形態としても実施できる。Pt－Mo合金－CeO_2担持担体またはPt－CeO_2担持担体は、Pt－Mo合金担持担体またはPt担持担体を微粒子状CeO_2と機械的に混合することによっても得られる。

【0007】さらに、本発明に係る燃料電池用カソード電極触媒の製造方法は、別の形態で、Sb_2O_3粉末を500℃以上で空気中で焼成し、Pt－Mo合金担持担体と機械的に混合し、Pt－Mo合金－Sb_2O_4担持担体を得るようにしている。本発明は、固体高分子型燃料電池に好適であるが、他にも、リン酸型燃料電池等の燃料電池に適用することもできる。

【0008】

【発明の実施の形態】以下、本発明に係る燃料電池用カソード電極触媒およびその製造方法をその実施の形態等についてさらに詳細に説明する。

【0009】燃料電池では、その一実施の形態として、固体高分子膜を挟んで燃料極側の白金触媒層と、空気極側の白金触媒層とを備えている。ここで、アノード（燃料極）、カソード（空気極）では、下記のような反応が行われる。

【0010】アノードにおいて白金触媒層により、以下の反応を起こさせる。

$H_2 \rightarrow 2H^+ + 2e^-$

この反応によって生じるH^+が拡散する。一方、カソードにおいて白金触媒層により、以下の反応を起こさせる。

$2H^+ + 2e^- + 1/2O_2 \rightarrow H_2O$

これらの反応を合わせて電池反応が構成され、起電力を得ることができる。

【0011】ここで、前記したように、カソード側の空気の還元反応の抵抗が大きく律速段階を構成しているものと思われる。本発明らは、白金触媒層に用いるＰｔ－Ｍｏ合金を用いた電極触媒について、鋭意検討した結果、さらにSb_2O_4とCeO_2から成るグループから選択した少なくとも一の助触媒を用いることによって、このような抵抗が大幅に減少することを見出した。その原理については、完全には裏付けられていないものの、ほぼ図1について以下に説明するところによると思われる。図１に示すように、まず、担体粒子１上の助触媒粒子２に酸素分子３が捕獲される。該酸素分子３は、Ｐｔ－Ｍｏ合金の粒子４中のＭｏ成分に引かれてＰｔ－Ｍｏ合金粒子４にスピルオーバーする。これによって、Ｐｔ成分の触媒特性が発揮され、酸素の還元反応が速やかに進行する。なお、本発明者らは、Sb_2O_4を助触媒とする場合には、Ｐｔ－Ｍｏ合金でなければ効果が確認できないのに対し、CeO_2で単にＰｔだけを担持した担体上に担持するだけで抵抗低減の効果を確認している。したがって、図１のメカニズムのように酸素のスピルオーバーは、CeO_2を用いた場合、Ｍｏがなくても進行するものと推測される。

【0012】前記担体の粉末は、炭素粉末が好ましく、例えば、黒鉛、カーボンブラック、電気導電性を有する活性炭等を挙げることができる。特に、燃料電池用電極触媒には、ケッチェンカーボン、バルカンカーボンが好ましい。

【0013】Ｐｔ－Ｍｏ合金を用いる場合、燃料電池用カソード電極触媒に含まれるＰｔ－Ｍｏ合金成分中のＭｏの比率は１～９９モル％、Ｐｔ－Ｍｏ合金をカーボンに担持した場合のＰｔ－Ｍｏ合金担持カーボン中のＰｔ－Ｍｏ合金の比率は、１～９９ｗｔ％であることが好ましい。また、Ｐｔ－Ｍｏ合金を用いる場合、助触媒としてのCeO_2、Sb_2O_4の担持量は、Ｐｔ－Ｍｏ合金担持カーボンの重量に対し、０．０１～１０倍が好ましい。

【0014】Ｐｔ－Ｍｏ合金ではなく、Ｐｔを用いる場合、Ｐｔをカーボンに担持した場合のＰｔ担持カーボン中のＰｔの比率は、１～９９ｗｔ％であることが好ましい。また、Ｐｔを用いる場合、助触媒としてのCeO_2、Sb_2O_4の担持量は、Ｐｔ担持カーボンの重量に対し、０．０１～１０倍が好ましい。

【0015】次いで、本発明に係る燃料電池用カソード電極触媒の製造方法について、カーボン担体に触媒活性成分を担持する場合を挙げてその実施の形態を説明する。

【0016】Ｐｔのモル量が所定の量になるようにＰｔ溶液を調製する。Ｐｔ溶液としては、H_2PtCl_6溶液、$Pt(NO_2)_2(NH_3)_2$等のＰｔ錯イオン溶液を挙げることができる。このＰｔ溶液を沸騰した水／エタノール混合溶液中に混合し、Ｐｔイオンを還元する。冷却後カーボン担体となるケッチェンカーボン等のカーボン粉末を添加し、カーボン粉末にＰｔを吸着担持させる。その後、ろ過、乾燥し、水素雰囲気中で熱処理し、Ｐｔ担持カーボンを得る。

【0017】次に、Ｐｔのモル数の０．１～２倍のＭｏ量の５塩化モリブデン水溶液等のモリブデン水溶液にＰｔ担持カーボンを含浸し、水素で２５０℃～８００℃で還元し、Ｐｔ－Ｍｏ合金担持カーボンを得る。次に、Ｐｔの重量に対して０．０１～１０倍のCeO_2を含むように硝酸セリウム水溶液等のセリウム水溶液をＰｔＭｏ担持カーボンに含浸し、空気中１５０～２００℃で焼成し、Ｐｔ－Ｍｏ合金－CeO_2担持カーボンを得る。

【0018】以上で、Ｍｏを担持せずに、Ｐｔの重量に対して０．０１～１０倍のCeO_2を含むように硝酸セリウム水溶液等のセリウム水溶液をＰｔ担持カーボンに含浸し、空気中で１５０～２００℃で焼成すれば、Ｐｔ－CeO_2担持カーボンを得ることができる。

【0019】また、Ｐｔ－Ｍｏ合金担持カーボンを得た後、CeO_2の代わりに、Sb_2O_4を担持させて、Ｐｔ－Ｍｏ合金－Sb_2O_4 担持カーボンを得ることができる。この場合、Ｐｔ－Ｍｏ合金担持カーボンの重量の０．０１～１０倍のSb_2O_4となるようにSb_2O_3粉末（粒径０．１μｍ以下）を５００℃以上で空気中で焼成し、Ｐｔ－Ｍｏ合金担持カーボンと機械的に混合し、Ｐｔ－Ｍｏ合金－Sb_2O_4担持カーボンを得ることができる。機械的に混合するのは、５００℃以上におけるSb_2O_4の焼成と同時に行うと、カーボン成分が燃えてしまうためである。

【0020】なお、Ｐｔ担持カーボン（Ｐｔ／Ｃ）、Ｐｔ－Ｍｏ合金担持カーボン（ＰｔＭｏ／Ｃ）は、市販品をそのまま用いることもできる。Ｐｔ－Ｍｏ合金－CeO_2担持カーボンはＰｔ－Ｍｏ合金担持カーボンに微粒子状CeO_2を機械的に混合して得ることもできる。

【0021】

【実施例】実施例１

Ｐｔのモル量が０．６ｍｍｏｌになるようにH_2PtCl_6溶液（Ｐｔ含有量１００ｇ／ｌ）を１ｇ金属／ｌに希釈した。イオン交換水１４４０ｇ、エタノール１１４０ｇ、ポリビニルアルコール０．４ｇの溶液を沸騰させた。この沸騰した溶液に、先に調製したＰｔイオン溶液を添加し、１５分（通常、１０分～２４時間）反応させ、Ｐｔイオンを還元した。冷却後、カーボン粉末（比表面積が８００m^2／ｇのケッチェンカーボン）１２０ｍｇを添加、撹拌し、カーボンにＰｔを吸着担持させた。その後、ろ過、乾燥し、水素雰囲気中で２５０℃、１時間（通常、０．５～６時間）熱処理し、ポリビニルアルコールを熱分解除去し、Ｐｔ担持カーボン触媒を得た。次に、Ｐｔのモル数の１倍（通常、０．１～２倍）

のＭｏ量の５塩化モリブデン水溶液にＰｔ担持カーボンを含浸し、水素で５００℃（通常、２５０℃～８００℃）で還元し、Ｐｔ－Ｍｏ合金担持カーボンを得た。次に、硝酸セリウム水溶液をＰｔ－Ｍｏ合金担持カーボンに含浸し、空気中２００℃で焼成し、Ｐｔ－Ｍｏ合金－CeO_2担持カーボンを得た。

【００２２】実施例２

Ｐｔのモル量が０．６ｍｍｏｌになるようにＨ２ＰｔＣｌ６溶液（Ｐｔ含有量１００ｇ／ｌ）を１ｇ金属／ｌに希釈した。イオン交換水１４４０ｇ、エタノール１１４０ｇ、ポリビニルアルコール０．４ｇの溶液を沸騰させた。この沸騰した溶液に、先に調製したＰｔイオン溶液を添加し、１５分（通常、１０分～２４時間）反応させ、Ｐｔイオンを還元した。冷却後、カーボン粉末（比表面積が８００m^2／ｇのケッチェンカーボン）１２０ｍｇを添加、攪拌し、カーボンにＰｔを吸着担持させた。その後、ろ過、乾燥し、水素雰囲気中で２５０℃、１時間（通常、０．５～６時間）熱処理し、ポリビニルアルコールを熱分解除去し、Ｐｔ担持カーボン触媒を得た。次に、Ｐｔの重量に対して２倍（通常、０．０１～１０倍）のCeO_2を含むように硝酸セリウム水溶液をＰｔ担持カーボンに含浸し、空気中２００℃で焼成し、Ｐｔ－CeO_2担持カーボンを得た。

【００２３】実施例３

Ｐｔのモル量が０．６ｍｍｏｌになるようにＨ２ＰｔＣｌ６溶液（Ｐｔ含有量１００ｇ／ｌ）を１ｇ金属／ｌに希釈した。イオン交換水１４４０ｇ、エタノール１１４０ｇ、ポリビニルアルコール０．４ｇの溶液を沸騰させた。この沸騰した溶液に、先に調製したＰｔイオン溶液を添加し、１５分（通常、１０分～２４時間）反応させ、Ｐｔイオンを還元した。冷却後、カーボン粉末（比表面積が８００m^2／ｇのケッチェンカーボン）１２０ｍｇを添加、攪拌し、カーボンにＰｔを吸着担持させた。その後、ろ過、乾燥し、水素雰囲気中で２５０℃、１時間（通常、０．５～６時間）熱処理し、ポリビニルアルコールを熱分解除去し、Ｐｔ担持カーボン触媒を得た。次に、Ｐｔのモル数の１倍（通常、０．１～２倍）のＭｏ量の５塩化モリブデン水溶液にＰｔ担持カーボンを含浸し、水素で２５０℃～８００℃で還元し、Ｐｔ－Ｍｏ合金担持カーボンを得た。次に、Ｐｔ－Ｍｏ合金担持カーボンの重量の２倍（通常、０．０１～１０倍）のSb_2O_4となるようにSb_2O_3粉末（粒径０．１μｍ以下）を５００℃以上で空気中で焼成し、Ｐｔ－Ｍｏ合金担持カーボンと機械的に混合し、Ｐｔ－Ｍｏ合金－Sb_2O_4担持カーボンを得た。

【００２４】実施例４

実施例1～３のカソード電極触媒を用いて固体高分子型燃料電池を製造し、その試験を行い、発電性能を評価した。

【００２５】（電池セルの調製）アノード電極触媒（ＰｔＲｕ合金担持カーボン）に水／エタノール混合液並びに高分子電解質溶液としてナフィオン溶液を添加して超音波攪拌にてスラリーを調製した。得られたスラリーをテフロン（登録商標）シートに塗布して膜厚５０μｍの固体高分子膜（デュポン社製で、商品名がナフィオン膜）の片面に転写し、アノード極を形成した。アノード極中のＰｔ量は０．５ｍｇ／ｃm^2で、Ｒｕ量は０．５ｍｇ／ｃm^2で、ナフィオン量は１ｍｇ／ｃm^2であった。

【００２６】一方、実施例１～３のカソード電極触媒に水／エタノール混合液並びに高分子電解質溶液としてナフィオン溶液を添加して超音波攪拌にてスラリーを調製した。得られたスラリーをテフロンシートに塗布して膜厚５０μｍの固体高分子膜（デュポン社製で、商品名がナフィオン膜）のアノードを転写した面と反対側の面に転写し、カソード極を形成した。カソード極中のＰｔ量は０．５ｍｇ／ｃm^2で、ナフィオン量は０．５ｍｇ／ｃm^2であった。アノード極及びカソード極それぞれにカーボンペーパを貼り付けた後、これらを１対のセパレータで挟み、５ｃｍ四方の電極セルを作製した。

【００２７】<発電性能評価>得られた電極セル１～３について、下記に説明する試験条件で発電試験を行い、その結果を下記表１に示す。

【００２８】アノード側：H_2 ６０％、CO_2 ２０％、N_2 ２０％、ＣＯ１０ｐｐｍ、２ａｔａ、温度８０℃、水素利用率８０％

カソード側：空気(Air)、２ａｔａ、温度８０℃、空気利用率４０％

【表１】

	0.15A/cm2	0.35A/cm2	0.7A/cm2
電極1	0.80 V	0.75 V	0.65 V
電極2	0.80 V	0.75 V	0.65 V
電極3	0.82 V	0.76 V	0.66 V
従来電極	0.78 V	0.70 V	0.60 V

【００２９】表１から明らかなように、試作触媒１～３を用いた電極セル１～３は、従来セルに比べ高性能であることがわかる。なお、上記実施例は、固体高分子型燃料電池について行った。しかし、本発明は、このようなものに限定されるものではなく、リン酸型燃料電池等の他の燃料電池にも適用することができる。

【００３０】

【発明の効果】上記したところから明らかなように、本発明によれば、カソードにおける酸素の還元反応の速度を上昇させるようにした燃料電池用カソード電極触媒およびその製造方法が提供される。

【図面の簡単な説明】

【図１】本発明における酸素の還元のメカニズムを説明する概念図である。

【符号の説明】

7

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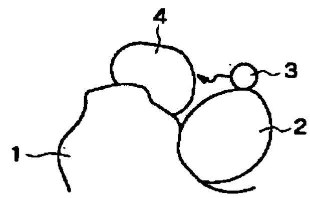
1　担体粒子　＊3　酸素分子
2　助触媒粒子　＊　4　合金粒子

【図１】



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